

ELECTROWINNING ANODES WHICH RAPIDLY PRODUCE A PROTECTIVE OXIDE COATING

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*now abandoned
pending.*

Field of the Invention

This invention relates to an improved electrowinning anode particularly for zinc electrowinning. The anode consists of a rolled lead-silver alloy, preferably a lead-calcium-silver alloy, with controlled surface grain structure. Because the anode is used in zinc electrowinning, it should contain no tin. The surface grain structure is formed by a combination of anode chemistry, rolling and heating, preferably while rolling. When placed in a zinc electrowinning cell, the anode surface is rapidly covered with an adherent oxide coating.

Background of the Invention

A zinc electrowinning tankhouse uses cast lead-silver alloy anodes. Silver is added to lead anodes for electrowinning to reduce the rate of corrosion of the anodes in use. Lead anodes used in zinc electrowinning generally contain 0.5-1.0% silver. Lead-silver anodes used for zinc electrowinning contain no tin because tin will plate on the negative anode and prevent zinc deposits.

To produce good quality zinc the cathode in an electrowinning cell must contain less than 10 ppm lead. In order to reduce lead contamination of the cathode, the lead anode must be coated with a protective layer of PbO_2/MnO_2 . The silver present in the anode decreases the rate of initial oxidation of the anode surface leading to an extended time period before a stable oxide film is produced. Conditioning new anodes by developing a PbO_2/MnO_2 layer on the surface normally takes many weeks. The complete formation of this layer may take as long as 60-90

1 days. Until the anode is fully conditioned, the zinc cathodes in electrowinning cells experience
high lead contents, high numbers of nodules and poor current efficiency. In addition, zinc
production is substantially reduced as manganese ions are recirculated between anode and cathode
as MnO_2 spalled off the anode is reduced at the cathode to produce MnSO_4 . The production of
5 zinc from a cell containing new unconditioned anodes may produce as much as one-third less zinc
than corresponding conditioned cells.

Once a stable layer of $\text{PbO}_2/\text{MnO}_2$ is formed on the anode, the current efficiency of the
zinc electrowinning process increases dramatically, and the lead contamination of the resultant
cathodes also decreases dramatically. Production of a stable PbO_2 or $\text{PbO}_2/\text{MnO}_2$ layer via
pretreatment of the anode is described by Ecgett *et al.* in U.S. Patent No. 3,880,733, Gaunce *et*
10 *al.* in U.S. Patent No. 3,392,094, Fountain *et al.* in U.S. Patent No. 3,755,112, as well as R.H.
Farmer in "Electrometallurgy" ed. H. Baker 1969. As described therein, a stable PbO_2
layer/ MnO_2 layer is typically created by the immersion of the anodes in a preconditioning solution
in which the anodes are electrolyzed to produce corroded layers. In some cases the anodes are
first immersed in water or water and air to produce a PbO , $\text{Pb}(\text{OH})_2$, or PbCO_3 film which is more
readily oxidized to a protective PbO_2 layer than the normal cast or rolled surface. Rodrigues and
17 Meyer, in "EPD Congress 1996" ed. G. Warren, describe the use of sandblasting to aid in
preconditioning anodes.

Lead-silver alloy anodes are relatively weak. In use, they can become warped and bent
leading to short circuits between the anode and cathode, low current efficiency, and lead
21 contamination of the cathodes in the area of the short circuit. To improve the mechanical
properties of the lead-silver anodes alloying elements such as calcium, strontium, barium and
others have been added to the anodes to improve the mechanical properties. For example, UK

1 patent application GB 2149424A by M.J. Thom teaches an alloy containing 0.4-1.0% Ag, 0.05-
0.15% Ca/Sr, less than 0.0002% antimony and optionally barium to reduce calcium losses during
remelting.

5 Production of cast lead-silver or lead-silver-calcium anodes often results in the formation
of numerous holes, voids or laps in the anode surface. In use, these can initiate internal corrosion
in localized areas which can weaken the anode and cause warping. When the anodes are
periodically cleaned of the adhering MnO_2 deposit, the internal corrosion may cause cracking
which can lead to premature anode failure.

9 To reduce the presence of internal porosity or laps, lead-silver or lead-calcium-silver alloys
have been rolled into sheets. These sheets have been joined to a copper busbar by various means
but primarily by welding the rolled sheet to lead which has been cast around the copper busbar.
The rolled sheet generally has a smooth surface on which it is more difficult for the $\text{PbO}_2/\text{MnO}_2$
corrosion product to produce an adherent film. In addition, the grain structure is uniform and is
oriented in the rolling direction producing a grain structure with few grain boundaries available
for corrosion and attachment of the oxidized film.

17 The improvement taught by this invention is the rolling of a cast billet of lead-silver alloys
and treatment of the alloy during or after rolling at a temperature sufficiently high to produce a
surface on which the $\text{PbO}_2/\text{MnO}_2$ layer more readily adheres due to a grain structure having many
grain boundaries. The grain structure is nonuniform (*i.e.*, not oriented in the rolling direction).
These anodes have more satisfactory mechanical characteristics than prior art cast anodes and can
21 be conditioned much more rapidly than prior art rolled anodes.

Summary of the Invention

This invention relates to a lead-silver anode for zinc electrowinning having a randomly oriented grain structure with many grain boundaries. The anode is formed by rolling a cast lead-silver alloy and heat treating the alloy either during or after rolling at a temperature sufficiently high to cause recrystallization of the alloy and to prevent most or all of any calcium, barium and/or strontium present in the alloy from precipitating from solution. Because the anode is used for zinc electrowinning it contains 0% tin. In anodes formed via this procedure, finely divided silver particles form during solidification and prevent gross grain structure growth while the high temperatures result in a material with a recrystallized grain structure with many grain boundaries. The material is also without stresses induced by rolling. A temperature greater than about 100°C and preferably above about 150°C is typically required to produce the proper grain structure.

Detailed Description of the Invention

In accordance with the invention, a lead-silver anode containing 0% tin for use in zinc electrowinning is formed preferably by rolling a cast lead-silver alloy at a temperature high enough to cause recrystallization of the alloy. The temperature is also high enough to prevent precipitation of any alloying elements, such as barium, calcium or strontium, during the rolling process. As a result, an alloy is formed having a grain structure with many grain boundaries to which the $\text{PbO}_2/\text{MnO}_2$ layer may adhere more readily than in prior art alloys rolled at lower temperatures.

A lead alloy suitable for use in the practice of the invention may contain as little as about 0.30-0.45% silver. A preferred alloy also contains no more than about 0.08% calcium and preferably at least 0.03% calcium. A more preferred alloy contains about 0.04-0.07% calcium

1 and about 0.3 to 0.5% silver, most preferably about 0.065% calcium and about 0.35% silver. The
alloy may contain other alloying elements, including barium, strontium and other materials which
enhance the mechanical properties of an anode. The alloy may also contain small amounts of
aluminum to reduce the oxidation of the reactive alloying elements. The alloy must not contain
5 any tin as tin will prevent zinc from depositing.

If the silver content of the lead alloy used to make the anode of the invention is too low,
there are insufficient silver particles to restrict the growth of the grains during the hot rolling
process. If the silver content is too high, the cost of the alloy is excessive.

9 If the calcium content of the lead alloy is too low, the improved mechanical properties
attributable to calcium will not be achieved. If the calcium content of the invention is higher than
about 0.08%, primary Pb_3Ca particles may precipitate from solution during the solidification
process and float to the surface of the billet. This will result in an enrichment in calcium on one
side of the rolled anode sheet compared to the remainder of the sheet. During use the side
enriched in calcium will corrode preferentially causing warping, short circuits, reduced current
efficiency and lead contamination of the cathode. The higher the calcium content of the anode
above 0.08%, the higher is the differential rate of corrosion between faces and the more likely
17 warping will occur in these rolled anodes.

If a billet is cast in a book mold prior to rolling from an alloy containing a calcium content
higher than 0.08%, the primary Pb_3Ca particles will form a layer near the center line. During
rolling the layer of particles will form a concentrated seam of calcium rich particles at the center
21 of the sheet. When the sheet is cut and assembled into anodes, the high calcium content central
areas will corrode preferentially causing delamination and fanning of the edges of the anode sheet.
These defects can cause short circuits as well as lead contamination of the cathode.

1 With calcium contents between about 0.03 and 0.08%, all the calcium remains in solution during the solidification process and the billet has a uniform calcium content throughout. Rolling this material at the preferred temperature produces a uniform grain structure consisting of silver particles in a matrix of lead and calcium.

5 An alternative method of forming the anode of the invention consists of cold rolling the cast alloy. The cold rolled anodes are treated by heating to a temperature of about 150°C or above. Heating removes the effects of the cold rolling and produces a grain structure on which a stable oxide film can be formed rapidly. If an anode sheet containing calcium is rolled below 9 100°C (cold rolling), some of the calcium can precipitate during the rolling operation. This precipitation, when combined with the silver content of the anode, can produce work hardening of the sheet. The hardened sheets can warp when some of the cold work is removed at tankhouse temperatures. Heating the anode sheet to a temperature above 150°C before use reverses the effects of calcium precipitation and the effects of cold rolling.

13 The grains of alloy sheets formed in accordance with the invention are randomly oriented instead of being oriented in the rolling direction, as is the case with prior art rolled alloys. This random orientation of fine grains with many grain boundaries presents a large grain boundary surface area in all regions of the surface. When an anode incorporating the rolled alloy is oxidized 17 to produce a $\text{PbO}_2/\text{MnO}_2$ layer, the oxidation is preferential to the grain boundaries and the $\text{PbO}_2/\text{MnO}_2$ product attaches itself to these grain boundaries and rapidly covers the adjacent surface. Therefore, the anodes of the present invention can be much more rapidly conditioned 21 than prior art anodes.

1 **Example**

 A lead-0.06% Ca-0.35% Ag alloy billet was hot rolled in a manner such that the temperature of the cast billet remained above 150°C during the rolling process. Sheets were attached to copper busbars via the process described by U.S. Patent No. 5,172,850. The resultant anodes were added as a full cell to a zinc electrowinning tankhouse. The anodes developed an adherent layer of PbO₂/MnO₂ within two days and produced high current efficiency and low cathode lead contents from the first week of operation.

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